

## FULL CONTENTS

---

[Claim(s)]

[Claim 1]It comes to laminate a coat layer which contains acrylic modification urethane resin at least on one side of a substrate film made of polyolefin system resin, And a lamination film made of polyolefin system resin whose ratios (tensile elastic modulus of the tensile elastic modulus / substrate film of a coat layer) to a tensile elastic modulus (JIS K7127) of this substrate film of a tensile elastic modulus (JIS K7127) of this coat layer are 1-4.5.

[Claim 2]Acrylic modification urethane resin Organic diisocyanate, the amount polyol of polymers, 80 to 40 weight % of acrylic components (B) which consist of 20 to 60 weight % of urethane resin (A) produced by making a chain elongation agent react, a radical polymerization nature unsaturated monomer, and/or its polymerization thing are copolymerized. The lamination film made of polyolefin system resin according to claim 1 which is \*\*\*\*\* acrylic modification urethane resin.

[Claim 3]The lamination film made of polyolefin system resin according to claim 2 whose amount polyol of polymers is a polycarbonate polyol of the molecular weights 1000-3000.

[Claim 4]A lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-3 whose hydroxyl value of this acrylic modification urethane resin acrylic modification urethane resin has a hydroxyl group, and is 5 - 30 KOHmg/g.

[Claim 5]a coat layer -- methyl ethyl ketone -- a lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-4 which contain a meltable ultraviolet ray absorbent and/or a hindered amine light stabiliser one to 30weight %.

[Claim 6]A lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-5 in which a coat layer contains the poly acrylic resin particles of 1-10 micrometers of mean particle sizes one to 30weight %.

[Claim 7]A substrate film made of polyolefin system resin A polyolefin system thermoplastic elastomer, At least one sort as which hydrogenation styrene butadiene copolymerization rubber and density are chosen from low density metallocene system polyethylene below  $0.900 \text{ g/cm}^3$ , A lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-6 containing gay polypropylene and random polypropylene.

[Claim 8]A lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-7 whose tensile elastic modulus of a substrate film made of polyolefin system resin is 200 - 900MPa.

[Claim 9]A lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-8 in which a substrate film made of polyolefin system resin is a layered product which has a inner layer, an intermediate layer, and an outer layer, and this intermediate layer contains colorant.

[Claim 10]An adhesion film made of polyolefin system resin in which an adhesive layer was laminated by one side of a lamination film made of polyolefin system resin given in any 1 paragraph of Claims 1-9.

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention]As for the adhesion film for an ornament (tape), the sticker [ this invention ] aiming at attachment on an adhesion film (tape), a signboard, several kinds of parts, etc. the object for Medical Science Division and for industry, a marking film, etc. are related with the lamination film made of polyolefin system resin to turn.

In detail, it excels in many performances, such as long-term durable performances, such as curved surface flattery nature, a sex with a crack-proof, and weatherability, adhesion nature, solvent resistance, and coat flattery nature, and is related with the lamination film made of polyolefin system resin which can be incinerated with the easy incineration system after use.

[0002]

[Description of the Prior Art]From the former, as films which an adhesion film (tape) turns for an ornament, such as a sticker aiming at attachment on an adhesion film (tape), a signboard, several kinds of parts, etc. the object for Medical Science Division, and for industry, and a marking film, pliability, The film made of polyvinyl chloride system resin which is excellent in resistance to scuffing, weatherability, etc. has been used abundantly.

[0003]However, since the film made of polyvinyl chloride system resin had the danger that hydrogen chloride gas etc. will be emitted, on the occasion of incineration and abandonment, in an easy incineration system, it could not process but there was a problem of reducing the endurance of an incineration system, further.

[0004]Then, although the method of easing an incineration burden by using the film made of polyolefin system resin as a substrate in recent years is tried, Compared with what used the conventional film made of polyvinyl chloride system resin as the substrate, pliability, resistance to scuffing, etc. were not enough, and especially the thing to acquire for both of curved surface flattery nature and resistance to scuffing equivalent to the film made of polyvinyl chloride system resin and also the product with which it is satisfied of durable performance over a long period of time was difficult.

[0005]For example, when laminating an adhesive layer on one side of the above-mentioned film made of polyolefin system resin and using it for it as pressure sensitive adhesive tape, the uniform extension characteristic in the process in which this pressure sensitive adhesive tape is stuck in accordance with a covering object, and the stress relaxation characteristic after being stuck serve as important performance, but. The film made of polyolefin system resin causes permanent modification partially, and tends to produce a necking phenomenon, and has the problem that a crack is easily attached at the time of construction.

[0006]Although the film made of elasticity system polyolefin system resin using various elastomers as a method of improving this was proposed, a sex with a crack-proof was not enough and there were other problems that solvent resistance and the workability at the time of construction were bad.

[0007]Although it is known that resistance to scuffing will improve by the method of laminating a bridge construction coat (hard court) on the surface of a substrate film, A publicly known bridge construction coat, for example, the coat produced by constructing a bridge, about about 10000-molecular weight acrylics polyol and organic diisocyanate

Blocking-proof, When it laminated to an elasticity system polyolefin substrate therefore it became a hard coat with many hard segment portions in consideration of adhesion nature, pliability was missing and it was inferior to coat flattery nature and adhesion nature, and when the stress by modification started or a long-term durability test was done, there was a fault which is easy to produce a crack easily. It was difficult to have a fault, like the urethane system bridge construction coat produced by constructing a bridge in polyester polyol etc. and organic diisocyanate is extremely inferior in a sex with a crack-proof, and to improve more simultaneously in both coat flattery nature and a sex with a crack-proof. [0008] Thus, the film made of polyolefin system resin for [ over a long period of time ] durability which has the performance which maintained moderate pliability equivalent to a polyvinyl chloride resin film, and was excellent in the sex with a crack-proof, etc. was not yet completed.

[0009]

[Problem to be solved by the invention] This invention can improve the problem of conventional technology mentioned above, can process it with an easy incineration system, has still more moderate pliability, and a curved surface and its construction nature (curved surface flattery nature) to bending are good, And it is in providing the polyolefin system resin film which was excellent in the sexes with a crack-proof at the time of construction, etc., and was excellent in many performances, such as adhesion nature, solvent resistance, weatherability, and coat flattery nature.

[0010]

[Means for solving problem] Namely, the place made into the gist of this invention, [ at least one side of the substrate film made of (1) polyolefin system resin ] It comes to laminate the coat layer containing acrylic modification urethane resin, [ the lamination film made of polyolefin system resin and (2) acrylic-modification urethane resin whose ratios (tensile elastic modulus of the tensile elastic modulus / substrate film of a coat layer) to the tensile elastic modulus (JIS K 7127) of this substrate film of the tensile elastic modulus (JIS K 7127) of this coat layer are 1-4.5 ] Organic diisocyanate, the amount polyol of polymers, 80 to 40 weight % of acrylic components (B) which consist of 20 to 60 weight % of acrylic modification urethane resin (A) produced by making a chain elongation agent react, a radical polymerization nature unsaturated monomer, and/or its polymerization thing are copolymerized. The lamination film made of polyolefin system resin given in the above (1) which is \*\*\*\*\* acrylic modification urethane resin, (3) The lamination film made of polyolefin system resin of a description and (4) acrylic-modification urethane resin have a hydroxyl group in the above (2) whose amount polyol of polymers is a polycarbonate polyol of the molecular weights 1000-3000, And the lamination film made of polyolefin system resin given in either of above-mentioned (1) - (3) whose hydroxyl values of this acrylic modification urethane resin are 5 - 30 KOHmg/g, (5) The lamination film made of polyolefin system resin with a coat layer given in either of methyl-ethyl-ketone above-mentioned [ which contains a meltable ultraviolet ray absorbent and/or hindered amine light stabiliser one to 30weight % ] (1) - (4), (6) The lamination film made of polyolefin system resin given in either of above-mentioned (1) - (5) in which a coat layer contains the poly acrylic resin particles of 1-10 micrometers of mean particle sizes one to 30weight %, The substrate film made of polyolefin system resin (7) A polyolefin system thermoplastic elastomer, At least one sort as which hydrogenation styrene butadiene copolymerization rubber and density are

chosen from low density metallocene system polyethylene below  $0.900 \text{ g/cm}^3$ , The lamination film made of polyolefin system resin given in either of above-mentioned (1) - (6) containing gay polypropylene and random polypropylene, (8) The lamination film made of polyolefin system resin given in either of above-mentioned (1) - (7) whose tensile elastic moduli of the substrate film made of polyolefin system resin are 200 - 900MPa, (9) The substrate film made of polyolefin system resin is a layered product which has a inner layer, an intermediate layer, and an outer layer, And this intermediate layer. [ colorant ] It consists in the adhesion film made of polyolefin system resin in which the adhesive layer was laminated by one side of the lamination film made of polyolefin system resin given in either [ to contain ] the lamination film made of polyolefin system resin given in either of - (8), and above-mentioned (1) (10) above-mentioned (1) - (9).

[0011]Hereafter, the details of this invention are explained.

[0012]

[Mode for carrying out the invention][ the lamination film made of polyolefin system resin of this invention ] It comes to laminate the coat layer which contains acrylic modification urethane resin on the substrate film made of polyolefin system resin, And the ratios (tensile elastic modulus of the tensile elastic modulus / substrate film of a coat layer) to the tensile elastic modulus (JIS K 7127) of this substrate film of the tensile elastic modulus (JIS K 7127) of this coat layer are 1-4.5. By laminating the coat layer which contains specific urethane resin on the substrate film made of polyolefin system resin (it is hereafter described as a "substrate film"), a sex with a crack-proof, The sex with a crack-proof of the lamination film made of polyolefin system resin, coat flattery nature, etc. become good, and it becomes difficult to produce a crack etc. by improving many performances, such as adhesion nature, solvent resistance, and weatherability, and a coat layer's pulling, and an elastic modulus and a substrate film pulling, and making a ratio with an elastic modulus into a specific value. The ratio of a tensile elastic modulus brings a result which modification of a coat layer is large and is inferior in a sex with a crack-proof by less than one. On the other hand, since the flattery nature of a coat is [ as opposed to / become / the rigidity of a coat / too much / strong / the growth of a substrate ] inferior when 4.5 is exceeded, there is a possibility of becoming causes, such as crack generating.

[0013]As polyolefin system resin used for the substrate film of this invention, the combined use mixture of polyethylene system resin, a polypropylene resin, and these and other synthetic resins is mentioned.

[0014]the copolymer (low density polyethylene (LDPE).) of the ethylene which makes the independent polymer of ethylene, and ethylene the main ingredients as polyethylene system resin, and other copolymerizable monomers These mixtures, such as high-pressure method low density polyethylene, line low density polyethylene (LLDPE), high-density polyethylene (HDPE), and an ethylene alpha-olefin copolymer (metallocene system polyethylene) produced by polymerizing using a metallocene system catalyst, can be illustrated.

[0015]As a polypropylene resin, an independent polymer (gay polypropylene), copolymers, these mixtures, etc. of propylene can be illustrated. As this copolymer, propylene, ethylene, a random copolymer (random polypropylene) with other alpha-OLEFIN or a block copolymer (block polypropylene), the block copolymer containing a

rubber composition, or a graft copolymer is mentioned.

[0016][ as the above-mentioned propylene and other copolymerizable alpha-OREFIN ] The thing of 4-12 has the preferred number of carbon atoms, for example, 1-BUTEN, 1-pentene, 1-HEKISEN, 1-HEPUTEN, 1-OKUTEN, 4-methyl 1-pentene, 1-decene, etc. are mentioned, and one sort or two sorts or more of the mixtures are used. Usually, as for especially the mixed rate of alpha-OREFIN, it is preferred to consider it as 2 to 6 weight % one to 10weight % to propylene.

[0017][ as other synthetic resins mixed with polyethylene system resin and/or a polypropylene resin ] For example, polyisoprene rubber, butadiene rubber, butyl rubber, propylene butadiene rubber, Diene system rubbers, such as acrylonitrile butadiene rubber and acrylonitrile polyisoprene rubber (elastomer), Ethylene propylene copolymerization rubber, ethylene propylene nonconjugated diene rubber, a low crystallinity propylene [ which is 100 or less g/J ] independent [ ethylene butadiene copolymerization rubber and the crystal heat of fusion ( $\Delta H$ ) ] polymer (product [ made from Idemitsu Petrochemistry ] Idemitsu TPO.) CAP by Ube Industries, Ltd., Ube Rexene make UT2115 grade, Polyolefin obtained by the multi stage polymerizing method (made in Sun Alomar ) [ KYATAROI and ] Mitsubishi Chemical make ZERASU and Tokuyama P.E.R. etc. -- etc. -- a polyolefin system thermoplastic elastomer. Styrene thermoplastic elastomers (the hydrogenation thing of these is included), such as styrene butadiene series thermoplastic elastomers, such as styrene butadiene copolymerization rubber (SBR) and a styrene butadiene block copolymer, and styrene isoprene copolymerization rubber, are mentioned.

[0018]A differential scanning calorimeter (DSC) is used with the crystal heat of fusion ( $\Delta H$ ), After carrying out resin once more than a melting point and carrying out melting, it is the value calculated from the crystal peak area on a DSC chart when it cools the speed for 10 \*\*/, The polyolefin obtained by the multi stage polymerizing method is a copolymer which comes to carry out the multi stage polymerization of a (i) hard segment and the (ii) soft segment in two or more steps in a reaction machine. As a hard segment, (i) A propylene independent polymeric block, Or 2 yuan or a 3 yuan copolymer block of a copolymer block with propylene and alpha-OREFIN, for example, propylene/ethylene, propylene / 1-BUTEN, propylene / ethylene / 1-BUTEN, etc., etc. is mentioned. As a (ii) soft segment, an ethylene independent polymeric block, Or 2 yuan or a 3 yuan copolymer block of a copolymer block with ethylene and alpha-OREFIN, for example, ethylene/propylene, ethylene / 1-BUTEN, ethylene / propylene / 1-BUTEN, etc., etc. is mentioned. Although 0-60 weight-section combination of these elastomer components can be carried out to 100 to polyethylene system resin and/or polypropylene resin 40 weight section, [ the elastomer components ] What made the polypropylene resin the subject as a substrate film is preferred, and what carries out 50-0 weight-section content of the resin other than a polypropylene resin to 50 to polypropylene resin 100 weight section is preferred. Although polyethylene system resin, an elastomer, etc. above-mentioned as resin other than a polypropylene resin are mentioned, At least one sort as which density is especially chosen from low density metallocene system polyethylene below  $0.900 \text{ g/cm}^3$ , a polyolefin system thermoplastic elastomer, and hydrogenation styrene butadiene copolymerization rubber is preferred.

[0019]Since a tensile elastic modulus becomes good [ what is 200 - 900MPa / the processability of a substrate film ], a substrate film is preferred, and also it is preferred

that it is 300 - 900MPa. A substrate film as such a substrate film, [ as a resinous principle ] 95 to 50 weight % of polypropylene resins which consist of 0 to 100 weight % of gay polypropylene, and 100 to 0 weight % of random polypropylene, and the thing containing 5 to 50 weight % of hydrogenation styrene butadiene copolymerization rubbers, 0 to 100 weight % of gay polypropylene. And that in which 90 to 20 weight % of polypropylene resins, the polyolefin system thermoplastic elastomer, and/or density which consist of 100 to 0 weight % of random polypropylene contain 10 to 80 weight % of low density metallocene system polyethylene below 0.900 g/cm<sup>3</sup> can be illustrated.

[0020]As for a substrate film, it is preferred to contain light stabilizer, such as an ultraviolet ray absorbent and/or a hindered amine light stabiliser (HALS), from a weatherproof viewpoint.

[0021]As an ultraviolet ray absorbent, ultraviolet ray absorbents, such as an ester salicylate system, a benzophenone series, a benzotriazole series, a cyanoacrylate system, and a triazine series, are mentioned, for example. Specifically as an ester salicylate system ultraviolet ray absorbent, phenyl salicylate, 4-t-butyl phenyl salicylate, etc. are mentioned. As a benzophenone series ultraviolet ray absorbent, 2 and 2'-dihydroxy 4-methoxybenzophenone, 2, such as - tetra-hydroxy benzophenone, 2, 2' - dihydroxy 4 and 4'-dimethoxy benzophenone, 2, 2', 4, and 4'2'-dihydroxy benzophenone series ultraviolet ray absorbents, 2-hydroxy 4-methoxybenzophenone, 2-hydroxy 4-n-octyloxybenzophenone, 2-hydroxy 4-methoxy 2'-KARUBOKISHI benzophenone, 2-hydroxy 4-benzoyloxy benzophenone, 2-hydroxy 5-KURORU benzophenone, 2-hydroxy benzophenone series ultraviolet ray absorbents, such as 2-hydroxy 4-methoxy 5-SURUHON benzophenone, 2, 4-dihydroxy benzophenone, \*\*\*\*\*- (2-methoxy 4-hydroxy 5-benzoyl phenyl) methane, etc. are mentioned.

[0022][ as a benzotriazole series ultraviolet ray absorbent ] (molecular weight 388), and, [ 2-[2'-hydroxy 3'-(3 "4" 5", and 6"-tetrahydro phthalimidomethyl)-5'-methylphenyl] benzodoria ] (molecular weight 448), and, [ 2-hydroxy 3 and 2-[5-bis(alpha and alpha-dimethylbenzyl)phenyl]-2H-benzodoria ] 2 2-methylene screw [4 - (1,1,3,3-tetramethylbutyl 6-(2H-benzotriazole-2-yl) phenol] (molecular weight 659) etc. are mentioned.) As a cyanoacrylate system ultraviolet ray absorbent, the 2-ethyl hexyl 2-cyano 3, 3-diphenyl acrylate, the ethyl 2-cyano 3, 3-diphenyl acrylate, the octyl 2-cyano 3, 3-diphenyl acrylate, etc. are mentioned.

[0023]As a triazine series ultraviolet ray absorbent, 2, 4-bis(2, 4-dimethylphenyl)-6-(2-hydroxy 4-n-octyloxy phenyl) 1,3,5-triazine, 2-(4, 6-diphenyl 1,3,5-triazine 2-IRU)-5 - (hexyl) (OKISHI)- Phenol, 2-(4, 6-bis(2, 4-dimethylphenyl)-1,3,5-triazine 2-IRU)-5-(octyloxy) phenol, 2-(4, 6-diphenyl 1,3,5-triazine 2-IRU)-5-(octyloxy) phenol, 2-(4, 6-bis(2, 4-dimethylphenyl)-1,3,5-triazine 2-IRU)-5-(HEKISHIROSHIKI) phenol and 2-(4, 6-diphenyl 1,3,5-triazine 2-IRU)-5-(methyl) (OKISHI) phenol are mentioned. Especially, that whose molecular weight it is an ultraviolet ray absorbent of a benzotriazole series or a triazine series, and is 300 or more at the point of being hard to blow off to the temporality of after substrate film surface is preferred. Especially the loadings of an ultraviolet ray absorbent should just be a category which is not restricted and does not blow off from a substrate film, and are about 0.05-5 weight sections to polyolefin system resin 100 weight section preferably.

[0024]As a hindered amine light stabiliser, 2, 2, 6, and 6-tetramethyl piperidyl 4-benzoate, Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)sebacate, Tris (2, 2, 6, and 6-

tetramethyl 4-piperidiny) phosphite ("KIMASOPU 944" by Ciba-Geigy), 1, 3, 8-bird \*\*\*\*- 7, 7, and 9, 9-tetramethyl 3-n-OKUCHIRUPIRO [4, 5] Deccan 2, 4-dione (the "tinuvin 144" by Ciba-Geigy), 1, 2, 3, 4-tetra (4-carbonyloxy 2, 2, and 6, 6-tetramethyl piperidyl)-butane, 1, 3, 8-bird \*\*\*\*- 7, 7, and 9, 9-tetramethyl 2, 4-dioxo SUPIRO [4, 5] Deccan, Bird (4-acetoxy 2, 2, and 6, 6-tetramethyl piperidyl) amine, 4-stearoyl \*\*\*\*\*- 2, 2, and 6, 6-tetramethylpiperidine, 4-benzyloxy 2, 2, and 6, 6-tetramethylpiperidine, the 4-phenylcarbamoxyloxy 2, 2, and 6, 6 tetramethylpiperidine, the 4-p-toluenesulfonyloxy 2, 2, and 6, 6-tetramethylpiperidine, Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)terephthalate etc. are mentioned. inside -- \*\*\*\* -- passing -- the time -- after -- a substrate -- a film -- the surface -- blowing off -- being hard -- saying -- a point -- a long period of time -- weatherability -- being good -- saying -- things -- from -- a molecular weight -- 1000 -- more than -- a thing -- using -- things -- desirable -- especially -- polyolefin -- hindered amine -- a frame -- having -- a compound -- copolymerizing -- having made -- a thing -- blowing off -- hard -- it is desirable . Especially loadings should just be a category which is not restricted and does not blow off from a substrate film, and are about 0.05-5 weight sections to polyolefin system resin 100 weight section preferably.

[0025]In addition to this on a substrate film, an antioxidant, colorant, a bulking agent, a slip additive (lubricant), an anti blocking agent, etc. can be added within limits which do not spoil its purpose and performance if needed.

[0026]As an antioxidant, a phenol system, a sulfide system, a phosphorus system, and an isocyanurate system antioxidant are mentioned.

[0027]If common organicity and inorganic pigment are mentioned as colorant and it has heat resistance at the temperature of around 300 \*\* which is the usual molding temperature of polyolefin system resin, according to the purpose, are selectable suitably, For example, azo (poly), a phthalocyanine system, the Indanthrene system, a dye rake system, Various inorganic pigments, such as oxide systems, such as various organic colors, such as a quinacridone series and a dioxazine system, and titanium oxide, a chromic acid molybdc acid system, a sulfide and a selenium ghost system, a Ferro cyanide system, calcium carbonate, and carbon black, are mentioned. Loadings are usually about 1-30 weight sections to polyolefin system resin 100 weight section.

[0028]Generally as a method of fabricating a substrate film, a publicly known film molding method is mentioned extrusion molding methods, such as T Di molding method, an inflation molding method, a calendar molding method, etc., for example. When a substrate film has a inner layer, an intermediate layer, and an outer layer, can use the method of pasting together each film (layer) fabricated as a method of laminating each layer with a laminating machine, and the method of carrying out sticking-by-pressure lamination simultaneously with film fabrication, but. The method of creating a lamination film simultaneously with fabrication with a multilayer T Di extrusion method can also reduce the number of processes, and is preferred.

[0029]Although the thickness of a substrate film is suitably chosen in consideration of resin composition, concealment nature, and the flattery nature of a curved surface, it is usually 40-200 micrometers.

[0030]Although the substrate film can also use a monolayer, it has a inner layer, an intermediate layer, and an outer layer at least, and that whose thickness of an intermediate layer is not less than 50% of the thickness of this whole film is preferred. When blending colorant with said substrate film, since the appearance of a film is not spoiled that

blending with an intermediate layer cannot carry out plate out of the colorant easily at the time of forming processing of a film and the hue of a film is stabilized, it is desirable. As for a substrate film, it is desirable to improve adhesion nature with a coat layer or an adhesive layer by surface modification, such as corona discharge treatment, ozonization, and flame processing.

[0031][ as acrylic modification urethane resin which constitutes the coat layer of the lamination film made of polyolefin system resin of this invention ] An acrylic polyol, polyether glycol, a polyester glycol, A polyether ester glycol, a polycarbonate glycol, a polyolefin glycol, The acrylic modification urethane resin which copolymerizes and shines the acrylic component which consists of the urethane resin produced by making organic diisocyanate and a chain elongation agent react to this, an unsaturated monomer, and/or its polymerization thing is mentioned using the various amount polyols of polymers, such as a silicon polyol, one or more sorts. When a coat layer turns into a surface coat of the lamination film made of polyolefin system resin, Since the sex with a crack-proof of a coat will become still better if the bridge is constructed with organic diisocyanate or its ADAKUTO objects, such as a polymer of a fatty series, alicycle fellows, or aromatic series diisocyanate, acrylic modification urethane resin is preferred. [0032]As for the content of this acrylic modification urethane resin of a coat layer, or its bridge construction object, it is preferred that it is 60 to 100 weight %.

[0033]The above-mentioned acrylic modification urethane resin has a hydroxyl group, and it is preferred that a hydroxyl value is 5 - 30 KOHmg/g. There is a possibility that a hydroxyl value may become less than 5 KOHmg/g does not cover the expenses of bridge construction density, but insufficient [ a sex with a crack-proof ]. On the other hand, even if it exceeds 30 KOHmg/g, bridge construction density does not improve-like proportionally, but there is a possibility of the variation per day of bridge construction coat physical properties becoming remarkable conversely, and worsening weatherability etc. over a long period of time.

[0034]Especially as acrylic modification urethane resin, organic diisocyanate, the amount polyol of polymers, The acrylic modification urethane resin produced by copolymerizing 80 to 40 weight % of acrylic components (B) which consist of 20 to 60 weight % of urethane resin (A) produced by making an end stop agent react a chain elongation agent and if needed, a radical polymerization nature unsaturated monomer, and/or its polymerization thing, Or since a coat flexible [ the bridge construction object which consists of any one or more etc. sorts of the polymer of this acrylic modification urethane resin, a fatty series, alicycle fellows, or aromatic series diisocyanate or its ADAKUTO object, etc. ], and tough is obtained, it is desirable. Also in it, [ as acrylic modification urethane resin ] Organic diisocyanate, the amount polyol of polymers, the radical polymerization nature double bond content compound that has one or more active hydrogen and one radical polymerization nature double bond in the same molecule, It is desirable at especially the point that meltable acrylic modification urethane resin can control molecular structure stably to the organic solvent which copolymerized urethane resin containing the radical polymerization nature double bond obtained from an end stop agent a chain elongation agent and if needed, and a radical polymerization nature unsaturated monomer.

[0035][ as an organic diisocyanate ingredient used by this invention ] Hexamethylene diisocyanate, lysinemethylester diisocyanate, Fatty series diisocyanate, such as 2, 4, and 4-



trimethyl hexamethylene di-isocyanate and dimer acid diisocyanate, An isophorone diisocyanate (IPDI), 4, and 4'-methylene screw (cyclohexyl isocyanate) (H12MDI), Alicycle fellows diisocyanate, such as omega and omega'-diisocyanate JIMECHIRU cyclohexane, Xylylene diisocyanate, tetramethyl xylylene diisocyanate, p-phenylene diisocyanate, tolylene diisocyanate (TDI), These two or more kinds of mixtures, such as aromatic series diisocyanate, such as 4 and 4'-diphenylmethane diisocyanate (MDI), NAFTA \*\*\*\*\* 1, 5-diisocyanate, and tolidine di-isocyanate, are mentioned.

[0036]Also in these, when thinking machinery intensity as important, and thinking aromatic series diisocyanate, such as MDI, and weatherability as important, alicycle fellows diisocyanate, such as IPDI, \*\*\*\*\* MDI, etc. are preferred.

[0037]As an amount polyol ingredient of polymers, a polycarbonate glycol, polyether glycol, a polyester glycol, a polyether ester glycol, a polyolefin glycol, a silicon polyol, etc. are mentioned, and a polycarbonate glycol is especially preferred. The poly butylene carbonate obtained from low-molecular quantity JIORU, alkylene carbonate, or dialkyl carbonate by a \*\* glycol or \*\* alcohol as a polycarbonate glycol, Polyhexamethylene carbonate, poly (3-methyl 1, 5-pentylene) carbonate, etc. are mentioned. What is produced by carrying out ring opening polymerization of the cyclic ether as polyether glycol, for example, polyethylene glycols, polypropylene glycol, a polytetramethylene glycol, etc. are mentioned. as a polyester glycol -- dicarboxylic acid (succinic acid and glutaric acid.) Adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, the anhydrides, such as phthalic acid, and low-molecular quantity JIORU (ethylene glycol.) Diethylene glycol, triethylene glycol, propylene glycol, A dipropylene glycol, 1, 2-butanediol, 1, 3-butanediol, 1, 4-butanediol, a polytetramethylene glycol, 1,5-pentanediol, 1, 6-hexandiol, 3-methyl 1,5-pentanediol, Neopentyl glycol, the 2-ethyl 1, 3-hexane glycol, 2, 2, 4-bird methyl 1, 3-pentanediol, 3, and 3-dimethylol heptane, All [ 1,9-NONANJI ], the 2-methyl 1, 8-octanediol, What is obtained by heavy condensation with cyclohexane dimethanol, screw hydroxy ethoxy benzene, etc., For example, the thing obtained by the ring opening polymerization of the lactone to low-molecular quantity JIORU, such as polyethylene horse mackerel PETO, polypropylene horse mackerel PETO, a polubutylene adipate, polyhexamethylene horse mackerel PETO, and poly butylene sebacate, For example, polycaprolactone, poly methyl BARERO lactone, etc. are mentioned. What carried out ring opening polymerization of the cyclic ether to the polyester glycol as a polyether ester glycol and the thing which carried out heavy condensation of polyether glycol and the dicarboxylic acid, for example, poly (polytetramethylene ether) Aji Pate etc., are mentioned. As a polyolefin polyol, a poly butadiene polyol, a \*\*\*\*\* poly butadiene polyol, a poly isoprene polyol, etc. are mentioned. A poly dimethylsiloxane polyol etc. are mentioned as a silicon polyol.

[0038]Two or more kinds of amount polyols of polymers may be mixed, and may use the above-mentioned thing.

[0039]the weight average molecular weight of the amount polyol of polymers -- usually - - 200-10000 -- desirable -- 500-6000 -- it is 1000-3000 more preferably. When pliability is scarce when a molecular weight is too small, and a molecular weight is too large, it is in the tendency for adhesion nature to fall.

[0040]the reaction charge of organic diisocyanate and the amount polyol of polymers -- NCO/OH (molar ratio) -- usually -- 1.01-10 -- it is 1.5-5 preferably. If this ratio is too small, it will become the tendency for the amount of hard segments to decrease and for a

sex with a crack-proof to fall. On the other hand, since solubility is in the tendency for it to be scarce and for viscosity to also become high too much when too large, it is not desirable.

[0041]The less than 500 usual molecular weight low-molecular diol compound used as materials of polyester polyol as a chain elongation agent, For example, ethylene glycol, diethylene glycol, triethylene glycol, Propylene glycol, a dipropylene glycol, 1, 2-butanediol, 1, 3-butanediol, 1, 4-butanediol, a polytetramethylene glycol, 1,5-pentanediol, 1, 6-hexandiol, 3-methyl 1,5-pentanediol, Neopentyl glycol, the 2-ethyl 1, 3-hexane glycol, 2, 2, 4-bird methyl 1, 3-pentanediol, 3, and 3-dimethylol heptane, Fatty series JIORU, such as all [ 1,9-NONANJI ], the 2-methyl 1, and 8-octanediol, Dialkanolamine, such as aromatic series system JIORU, such as alicycle fellows JIORU, such as cyclohexane dimethanol, a KISHIRIREN glycol, screw hydroxy ethoxy benzene, screw hydroxyethyl terephthalate, and bisphenol A, and N-methyl di ethanol amine, etc. are mentioned. 2 and 4- or 2, 6-bird range amine, KISHIRI range amine, Aromatic diamine, such as 4,4'-diphenyl METANJI amine, ethylene diamine, 1, 2-propylene diamine, 1, 6-hexane JIAMIN, 2, and 2-\*\*\*\*\*- 1,3-propanediamine, The 2-methyl 1, 5-pen TANJI amine, 2 and 2, 4- or 2 and 4, 4-bird methylhexane JIAMIN, 2-butyl 2-ethyl 1,5-pen TANJI amine, 1,8-octane JIAMIN, Fatty series Gia Min, such as 1,9-NONANJI amine, 1, 10-DEKANJI amine, and ISOHO lounge amine, The 1-amino 3-aminomethyl 3 and 5, 5-trimethylcyclohexane (IPDA), 4, 4' - dicyclohexyl methanediamine (\*\*\*\* MDA) and isopropylidene cyclohexyl 4 and 4'-Gia Min, Low-molecular diamine compounds, such as alicyclic Gia Min, such as 1, 4-JIAMINO cyclohexane, 1, 3-screw aminomethyl cyclohexane, and tricyclodecane JIAMIN, are mentioned. These chain elongation agents can also be used as two or more kinds of mixtures. A part of polyols, such as TORIMECHI roll propane and glycerin, can be used together.

[0042][ as an end stop agent used by necessity ] Methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, Monoalcohol, such as n-butyl alcohol and isobutyl alcohol, Alkanol amine, such as monoamines, such as monoethyl amine, n-propylamine, JIECHIRU amine, G n-propylamine, and a G n-butylamine, monoethanolamine, and JIETANORU amine, etc. are mentioned.

[0043][ one or more active hydrogen and one radical polymerization nature double bond ] [ as a radical polymerization nature double bond content compound which it has in the same molecule ] Allyl alcohol, ARIRU amine, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, glycerin monoacrylate, Glycerin mono-methacrylate, glycerin monoallyl ether, These epsilon-KAPURO lactone additions, such as TORIMECHI roll propane monoacrylate and TORIMECHIRORU propane mono-methacrylate, gamma-methyl BARERO lactone addition, an ethylene oxide addition, a propylene oxide addition, etc. are mentioned. Two or more kinds of these mixtures may be sufficient. [ by using a compound which has two or more active hydrogen and one radical polymerization nature double bond in the same molecule especially ] It is effective in being able to introduce a pendant-like radical polymerization nature double bond into a urethane resin main chain, enabling polymer to introduce into a polyurethane chain as a graft chain in the shape of a pendant, and compensating a fault with other polymer taking advantage of original character of urethane resin.

[0044]content in urethane resin of a radical polymerization nature double bond -- usually

-- 1-200microeq/g -- desirable -- 10-150microeq/g -- it is 20-100microeq/g still more preferably. Content of a double bond may become compatibility of less than one piece is [ per less than 1microeq/g 1 million, i.e., a molecular weight, ] insufficient, and poor [ solution quality and coat quality ]. When more [ per molecular weight 5000 ] than one piece when content of a double bond exceeds 200microeq/g namely, there is a tendency which a ratio of reaction to 2 organic functions is high, and three-dimensions-becomes easy to seize at the time of a radical polymerization.

[0045] Manufacture of urethane resin in this invention is performed by the one shot method, a pre polymer-ized method, etc. in accordance with a publicly known method. As a solvent at the time of manufacturing urethane resin, usually Methyl ethyl ketone, Ketone, such as methyl isobutyl ketone and cyclohexanone, ethyl acetate, Ester, such as butyl acetate and acetic acid cello SORUBU, benzene, toluene, Hydrocarbon, such as xylene and hexane, diacetone alcohol, isopropanol, Some alcohols, such as the second butanol and the third butanol, a methylene chloride, Two or more kinds of these mixtures, such as aprotic polarity solvents, such as ether, such as chlorides, such as dichloroethane, a tetrahydrofuran, and diethylether, DIMETHYL formamide, dimethylsulfoxide, and N-methyl pyrrolidone, are used. The usual urethane-ized reaction catalyst is used as a catalyst at the time of manufacturing urethane resin. For example, the third class amine systems, such as iron systems, such as tin systems, such as dibutyltin dilaurate, a ZINC DIBUTYL DILAURATE rate, Djibouti rutin dioctoate, and stannous octoate, iron acetylacetonate, and ferric chloride, triethyl amine, and a triethylene diamine, etc. are mentioned. As a weight average molecular weight of the above-mentioned urethane resin in this invention, it is usually the range of 5000-200000. desirable -- 10000-150000 -- it is 15000-100000 still more preferably. It is in a tendency which is inferior in the coat physical properties of acrylic modification urethane resin which will be obtained if this weight average molecular weight is too small. If a weight average molecular weight is too large, compatibility with an acrylic component will be scarce and solution quality will fall. Since solution viscosity becomes high, it is in a tendency which is inferior in coating work nature. [ as a constituting-acrylic component radical polymerization nature unsaturated monomer ] Acrylic acid, meta-acrylic acid (it is hereafter described as "acrylic acid (meta)" collectively), (Meta) Derivatives, these mixtures, etc. of acrylic acid are mentioned, and specifically Acrylic acid (meta), (Meta) Methyl acrylate, ethyl acrylate (meta), butyl acrylate (meta), (Meta) Acrylic acid 2-ethylhexyl, acrylic acid (meta) lauryl, (Meta) Two or more kinds of these mixtures, such as acrylic (meta) monomers, such as acrylic acid cyclohexyl, acrylic acid (meta) tetrahydrofurfuryl, acrylic acid (meta) 2-hydroxyethyl, and acrylic acid (meta) 4-hydroxy butyl, are mentioned.

[0046] Manufacture of acrylic modification urethane resin of this invention for example, How to carry out the graft copolymerization of the radical polymerization nature unsaturated monomer to the urethane resin which contains a radical polymerization nature double bond so that it may be illustrated by JP,4-159318,A, JP,5-43756,B, JP,7-78105,B, JP,9-268215,A, etc., JP,5-262846,A, the method of carrying out addition condensation of the acrylic macromere which has active hydrogen so that it may be illustrated by JP,5-262847,A to urethane resin, What is necessary is just to depend a radical polymerization nature unsaturated monomer on the method of polymerizing, etc. under existence of the urethane resin which has at least one IIAZO combination in a molecule so that it may be illustrated by JP,2-229873,A. It is possible to copolymerize

also by reacting the radical polymerization thing of the above-mentioned radical polymerization nature unsaturated monomer to urethane resin materials. For example, in JP,H5-262847,A, the method of reacting an end dihydroxy macroscopic monomer to an organic diisocyanate compound using the mercaptan system chain transfer agent which has two hydroxyl groups and one mercapto group is introduced. As a mercaptan system chain transfer agent in this case, 1-Mel Caputo 1, all [ 1-METANJI ], all [ 1-ETANJI / 1-Mel Caputo 1 and ] and CHIOGU -- a lycee -- a phosphorus, 2-Mel Caputo 1, and all [ 2-pro pansy ]. All [ 3-pro pansy / the 2-Mel Caputo 2-methyl 1 and ], the 2-Mel Caputo 2-ethyl 1, all [ 3-pro pansy ], All [ 3-pro pansy / all / 3-pro pansy / all / 2-pro pansy / 1-Mel Caputo 2 and /, the 2-MERUKAPUTO ethyl 2-methyl 1, and /, the 2-MERUKAPUTO ethyl 2-ethyl 1, and ] etc. is mentioned. It is also possible to polymerize beforehand and to use as macromere the monomer which has a radical polymerization nature unsaturated bond and isocyanate groups, such as methacryloiloxy-ethyl isocyanate. Copolymerization with urethane resin and an acrylic component is performed by adding and heating the bottom of inactive gas air currents, such as nitrogen, the inside of an organic solvent, and a polymerization initiator by the usual solution polymerization method. As an organic solvent used, methyl ethyl ketone, methyl isobutyl ketone, Ester, such as ketone, such as cyclohexanone, ethyl acetate, butyl acetate, and acetic acid cello SORUBU, Hydrocarbon, such as benzene, toluene, xylene, and hexane, methanol, Ethanol, butanol, diacetone alcohol, isopropanol, Alcohols, such as the second butanol and the third butanol, a methylene chloride, Two or more kinds of these mixtures, such as aprotic polarity solvents, such as ether, such as chlorides, such as dichloroethane, diethylether, and a tetrahydro franc, JIMECHIRU formamide, dimethylsulfoxide, and N-methyl pylori boss, are mentioned. The resin solid content concentration at the time of a polymerization is usually 10 to 80 weight % preferably five to 95weight %. As a polymerization initiator, azobis isobutyronitrile, benzoyl peroxide, peroxidation JI t-butyl, KUMEN hydroperoxide, etc. are mentioned. The amount of addition of a polymerization initiator is usually 0.001 to 10 weight % to a radical polymerization nature monomer. 10-160 \*\* of polymerization temperature is 30-140 \*\* preferably.

[0047]As for the wt. ratio of the urethane resin (A) which constitutes acrylic modification urethane resin, and an acrylic component (B), it is preferred that it is urethane resin (A) / acrylic component (B) = 20 / 80 - 60/40. If there is much urethane resin (A), it will become a tendency which is remarkably inferior in a sex with a crack-proof. On the other hand, since coat flattery nature will be extremely inferior and will cause crack generating if there are many acrylic components (B), it is not desirable.

[0048]the weight average molecular weight of acrylic modification urethane resin -- usually -- 15000-200000 -- it is 20000-100000 still more preferably.

[0049]A crosslinking agent can be used for this invention in order to improve the coat intensity of acrylic modification urethane resin if needed. as a crosslinking agent, the ADAKUTO object of a fatty series, alicycle fellows, an aromatic series diisocyanate polymer, or this diisocyanate polymer mentions -- having -- any these one or more sorts can be used. The fatty series in the organic diisocyanate specifically mentioned in explanation of the above-mentioned urethane resin as this crosslinking agent, It is mentioned by the isocyanurate polymer of alicycle fellows or aromatic series diisocyanate, and, [ as an ADAKUTO object ] The ADAKUTO object which carried out addition condensation of these fatty series, alicycle fellows or aromatic series

diisocyanate, ethylene glycol and propylene glycol, hexane triol, the trimethylolpropanetrimethacrylate, etc. is mentioned.

[0050]The mixture ratio of acrylic modification urethane resin (base resin) and a crosslinking agent usually carries out 10-30 weight-section use of the crosslinking agent preferably five to 50 weight section to base resin 100 weight section.

[0051]It is made to dissolve in a solvent, and these base resin and crosslinking agents are used, and also usually it mixes and uses for suitable concentration using a dilution solvent etc.

[0052]As for the lamination film made of polyolefin system resin of this invention, it is preferred to blend light stabilizer, such as an ultraviolet ray absorbent and/or a hindered amine light stabiliser, with a coat layer in order to satisfy the weatherability under the long period of time in the outdoors and severe conditions.

[0053]and as an ultraviolet ray absorbent, [ 2-(2'-hydroxy 3' lauryl 5'-methylphenyl) benzodiora ] The condensation thing of methyl 3-[3-t-butyl 5-(2H-benzotriazole-2-yl)-4-hydroxyphenyl] propionate polyethylene glycols, They are mentioned by the hydroxyphenyl benzobird azole derivative etc. and, [ as a hindered amine light stabiliser ] Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)sebacate, Bis(1, 2, 2, 6, and 6-pentamethyl 4-piperidyl)sebacate, A 2-(3, 5-G t-butyl 4-hydroxybenzyl)-2-n-butyl malonic acid screw (1, 2, 2, 6, and 6-pentamethyl 4-piperidyl), Succinate dimethyl 1-. (2-hydroxyethyl)-4-hydroxy 2, 2, and 6, 6-tetramethylpiperidine pile condensation thing, and poly [{6-(1,1,3,3-tetramethylbutyl) amino 1,3,5-triazine 2 and 4-diyl} -- {(2, 2, and 6.) 6-tetramethyl 4-piperidyl -- imino --} hexamethylene {(2, 2, 6, and 6-tetramethyl 4-piperidyl) imino}] etc. are mentioned.

[0054]the inside of it -- methyl ethyl ketone -- the ultraviolet ray absorbent and hindered amine light stabiliser liquefied at a meltable thing, especially normal temperature of the dispersibility to coating liquid and compatibility with resin are preferred at a good point.

[0055]As for the loadings of an ultraviolet ray absorbent or a hindered amine light stabiliser, even when independent respectively or it uses together, it is preferred that it is 1 to 30 weight % among a coat layer. If there are few loadings, there is a possibility that the minute crack, a cave-in, or omission of a coat may be seen by a severe weathering test (it irradiates with ultraviolet rays for example, by super UV examination for 600 hours), and gloss may fall, and it is not desirable. On the other hand, since solvent resistance and performance with a crack-proof will fall with the fall of the degree of bridge construction of a coat, etc. if there are too many loadings, it is not desirable.

[0056]When using together, the mixed rate in particular does not limit, but it is usually ultraviolet ray absorbent/hindered amine light stabiliser = 3 / 1 - 1/2 (weight ratio).

[0057]Additive agents, such as a grinding agent of an organic system, lubricant, and metallic tone metallic powder, can be blended with the coat layer of this invention for the purpose on gloss control, a disposition with a crack-proof, and a design disposition.

[0058]As grinding agent and lubricant, the polyurethane resin particles for which a bridge is not constructed [ the poly acrylic resin particles for which a bridge is not constructed / bridge construction of the particulates of 1-10 micrometers of mean particle sizes or /, bridge construction, or ], and polycarbonate resin particles are mentioned. In addition, unsaturated fatty acid amide, such as saturated fatty acid amide, such as lauric acid amide and octadecanamide, erucic acid amide, and oleic amide, is mentioned. Addition of the poly acrylic resin particles is preferred at the point which improves a sex with a crack-

proof also in this. As for the amount of addition, it is preferred to use it so that it may become 1 to 30 weight % in a coat layer, and it should just use it in proper quantity in consideration of the surface gloss for which it asks, hue, a sex with a crack-proof, weatherability, etc.

[0059]What is necessary is to choose from from suitably and just to combine, while describing above resin composition of a substrate film, and resin composition of the coat layer so that the ratio of the tensile elastic modulus of a substrate film and a coat layer might be set to 1-4.5 in order to obtain the lamination film made of polyolefin system resin of this invention.

[0060]Coat formation on a substrate film the mixture which dissolved acrylic modification urethane resin in the publicly known organic solvent, and blended the crosslinking agent as occasion demands, [ a substrate film ] It coats by publicly known methods, such as a knife coat, a roll coat, or a photogravure roll coat, subsequently a hot air dryer etc. are used, and it carries out by heating several - minutes during several seconds, and making it usually dry and harden at 50-200 \*\*. 0.3-5 micrometers of thickness of the coat layer after dryness are 1-3 micrometers preferably. If thickness is thin, coat intensity is insufficient, and there is a possibility that a sex with a crack-proof, solvent resistance, and weatherability may not be satisfied. On the other hand, since there is a possibility of causing aggravation of pliability or curved surface flattery nature when thick, it is not desirable.

[0061]Thus, after giving corona discharge treatment and an anchor coat to one side (it is the opposite field when the coat layer is formed only in one side) of the lamination film made of polyolefin system resin of obtained this invention if needed, By providing an adhesive layer, the adhesion films for an ornament (tape) aiming at attachment on the adhesion film the object for Medical Science Division and for industry (tape), a signboard, several kinds of parts, etc., such as a sticker and a marking film, are obtained.

[0062]The kind in particular of adhesive is not limited and, for example A crude rubber system, A synthetic rubber system, acrylic, a urethane system, a vinyl ether system, a silicone series, An amide system, a styrene system adhesive, a styrene system elastomer, an olefin system elastomer, Various adhesives, such as \*\*\*\*\* olefin resin by which graft denaturation was carried out with ethylene system unsaturated carboxylic acid or its anhydride, may be used suitably, and the form may be any, such as a solution type, an emulsion type, and a hot melt type. In said adhesive layer, for the purpose of control of the adhesion characteristic, etc., if needed For example, alpha-pinene and beta-pinene polymer, Terpene series resin, such as a diterpene polymer and alpha-pinene phenol copolymer, Suitable adhesion grant agents, such as hydrocarbon system resin, such as a fatty series system, an aromatic series system, a fatty series, an aromatic series copolymer system, other rosin system resins and KUMARON indene series resin, phenol resin (ARUKIRU), and xylene series resin, can be blended. Softeners, such as liquefied polymer and paraffine system oil, a bulking agent, paints, an antiaging agent, stabilizer, an ultraviolet ray absorbent, etc. can blend required various additive agents according to a use etc.

[0063]

[Working example]Although the embodiment of this invention is used and explained for a work example in full detail below, this invention is not limited to the following work examples, unless the gist is exceeded.

The weight average molecular weight TOSOH CORP. make HLC8020 type gel permeation chromatography (GPC) device of <valuation method> (1) acrylic-modification urethane resin (coating liquid base resin) is used, The tetrahydro franc (THF) was used for the solvent and it developed in Showa Denko K.K. make column KF806L.

[0064]The obtained result was denoted by the weight average molecular weight (Mw) on the basis of a polystyrene correlation sample.

(2) The tensile elastic modulus of the film was measured according to tensile elastic-modulus JIS K 7127.

[0065]However, the dumbbell was carried out by No. 1 and tensile speed was carried out by a part for 50-mm/.

[0066]About a coat (film), to commercial mold-releasing paper, coating liquid is coated using a reverse roll coater so that coat thickness may be set to 10 micrometers, It heat-treated for 60 seconds within a 100 °C hot air dryer continuously, and mold-releasing paper was removed, the 10-micrometer-thick coat (film) was created, and the tensile elastic modulus was measured about this film.

(3) Load was removed and taken out after maintenance for 10 minutes under 100% growth modification on the above-mentioned tensile test conditions using the strip specimen with a necking characteristic width of 10 mm.

[0067]The existence of peeling of (%) and the transformation ratio (the length of the film before the length-examination of the film after an examination) of a film (the length of the film before x100-/examination), a modification state, and a coat was observed under the microscope etc., and it judged by the following rank.

[0068]O : it is changing uniformly and the transformation ratio after \*\*\*\*\* is less than 30%.

[0069]With no coat peeling.

[0070]\*\*: The transformation ratio after those with a neck and \*\*\*\*\* is 30 to 50% slightly.

[0071]x: -- a neck -- it is remarkable and the transformation ratio after \*\*\*\*\* exceeds 50%.

[0072]Generating and coat peeling have a detailed crack.

(4) Only the amount of modification was changed by the same examining method as the coat flattery nature above-mentioned necking characteristic, and the specimen fixed to the adhesion substrate in the state where it held under 10% growth modification was created. The specimen was observed under the microscope (100 times), and the existence of peeling of a coat and detailed crack generating was judged.

[0073]: Good changeless.

[0074]x: There is generating of a detailed crack and peeling of a coat is accepted.

(5) Using \*\*\*\*\* Science tabulation planar measurement machine with a crack-proof, the tip part set the cheesecloth of \*\* No. 3 which is not in \*\*\*\*\* which is 20 mm in diameter, and carried out 200 round-trip (part for 120-cm/in speed) friction of the coat surface of a lamination film under 1 kg of fixed load.

[0075]Visual observation of the surface state after an examination was carried out, and the rank of the following 1-5 estimated.

[0076]5: There is almost no crack.

[0077]4: A scratch-like crack is accepted slightly.

[0078]3: It is not conspicuous although a scratch-like crack is accepted.

[0079]2: A scratch-like crack is and is conspicuous.

[0080]1: A scratch-like crack is remarkable and poses a problem practically.

(6) The weatherproof super UV examination and the sunshine WEZARO meter examination were carried out.

[0081]The super UV examination performed ultraviolet exposure 5 hour /, and dew condensation 1 hour by turns using the SUV-W11 type by the Iwasaki Electric Co., Ltd. at ultraviolet-rays intensity/cm<sup>2</sup> of 85 mW ]<sup>2</sup> and black panel temperature of 63 °C of 295-450 nm, and 70% of humidity.

[0082]The sunshine WEZARO meter (SWOM) examination carried out the black panel temperature of 63 °C, and a water spray for 12 minutes every 60 minutes using the Suga Test Instruments WEL-SUN-HC type.

[0083]The appearance (gross, crack existence, dirt) change by the irradiation time indicated to table-1 was judged.

138 °C of <manufacture (a) of substrate film made of polyolefin system resin> melting points, Propylene ethylene random copolymer (: random polypropylene) 90 weight section of rate of bending flexibility 700MPa, hydrogenation styrene butadiene copolymerization rubber (styrene content 10wt%.) The resin composition which mixed ten weight sections and hindered amine light stabiliser (CHIBA Specialty Chemicals KIMASOBU 944) 0.1 weight section rate of hydrogenation >90% is used as a base for MFR3.5g/10 minutes, The 0.1-mm-thick substrate film made of polyolefin system resin was created with the extrusion molding machine by Mitsubishi Heavy Industries, LTD. using the coloring polypropylene resin constituent which mixed and prepared carbon black pigment 1 weight section.

[0084]Next, corona treatment of both sides of the substrate film made of polyolefin system resin was carried out, and the substrate film (a) of double-sided corona treatment was obtained.

[0085]The NURE index of these obtained substrate film (a) both sides was about 450microN.

[0086](b) 160 °C of melting points, gay polypropylene 60 weight section of rate of bending flexibility 1400MPa, 140 °C of melting points, ethylene propylene copolymer (: multi stage polymerization type polyolefin) 40 weight section of rate of bending flexibility 200MPa, The resin composition which mixed hindered amine light stabiliser (CHIBA Specialty Chemicals KIMASOBU 944) 0.1 weight section is used as a base, The coloring polypropylene resin constituent which mixed and prepared carbon black pigment 1 weight section is used, Like the above (a), the 0.1-mm-thick substrate film made of polyolefin system resin was created with the extrusion molding machine by Mitsubishi Heavy Industries, LTD., subsequently corona treatment of both sides of the substrate film made of polyolefin system resin was carried out, and the substrate film (b) of double-sided corona treatment was obtained.

[0087]The NURE index of these obtained substrate film (b) both sides was about 430microN.

[0088](c) 160 °C of melting points, gay polypropylene 40 weight section of rate of bending flexibility 1400MPa, 138 °C of melting points, propylene ethylene random copolymer (: random polypropylene) 40 weight section of rate of bending flexibility 700MPa, the low crystallinity propylene independent polymer (a polyolefin system thermoplastic elastomer.) of 160 °C of melting points Amount of crystal heat of fusion



\*\*H;50 g/J, rate of bending flexibility;500MPa20 weight section, The polypropylene resin constituent which mixed hindered amine light stabiliser (Ciba-Geigy KIMASOPU 944) 0.1 weight section is used as a base, The 0.1-mm-thick substrate film made of polyolefin system resin was created with the extrusion molding machine by Mitsubishi Heavy Industries, LTD. using the coloring polypropylene resin constituent which mixed and prepared carbon black pigment 1 weight section.

[0089]Next, corona treatment of both sides of this lamination film was carried out, and the substrate film (c) of double-sided corona treatment was obtained.

[0090]The NURE index of these obtained substrate film (c) both sides was about 480microN.

Isophorone diisocyanate 31.4 weight section is taught into the 4 TSU mouth flask furnished with the work-example 1 <manufacture of coating liquid base resin> stirrer, a channeling-back condensator, a tap funnel, and a thermometer, polycarbonate JIORU (plaque cell CD220 and a hydroxyl value -- 56.1 KOHmg/g) which carried out melting while heating and agitating at 90 \*\*. Daicel Chemical Industries, Ltd. make 128.4 weight section, glycerin mono-methacrylate (Blemmer GLM, Nippon Oil & Fats Co., Ltd. make) 2.2 weight section, and methyl hydroquinone 0.02 weight section were dropped in about 1 hour. After keeping the internal temperature at 90 \*\* and making it react for 4 hours, methyl-ethyl-ketone 208.9 weight section was added, and it agitated for 1 hour and diluted with 60 \*\*. Next, the solution of bottom ISOHO lounge amine of churning 8.7 weight section and isopropanol 52.2 weight section was dropped in 1 hour, and also G n-butylamine 3.3 weight section was added, and the end was blocked. Then, methylmetaacrylate 157.9 weight section, 2-hydroxyethyl methacrylate 16.1 weight section, Methyl-ethyl-ketone 385.4 weight section was taught, it heated at 70 \*\* under the nitrogen air current, azobis isobutyronitrile 5.2 weight section was trichotomized, and it added with one time interval, and also reacted for 10 hours. The obtained acrylic modification urethane resin solution (base resin solution) was viscosity 500 mPa-s of 35 weight % of resin solid content concentration, and this resin solution, and the weight average molecular weight 47000 of resin.

[0091]It is attached to base resin solution 100 weight section manufactured by the <manufacture of coating liquid> above, and solution of a hexamethylene di-isocyanate polymer 75weight % as a crosslinking agent Seven weight sections, A condensation thing of methyl 3-[3-t-butyl 5-(2H-BENSO triazole-2-yl)-4-hydroxyphenyl] propionate polyethylene glycols as 80 weight sections and also an ultraviolet ray absorbent for methyl ethyl ketone as a solvent ingredient 2.5 weight sections, 2.5 weight sections of bis(1, 2, 2, 6, and 6-pentamethyl 4-piperidiny)sebacate was mixed as a hindered amine light stabiliser, and coating liquid of about 21 weight % of solid content concentration was prepared.

[0092][ on a corona treatment side of one side (the surface side) of a substrate film made of <coating processing of substrate film made of polyolefin system resin> polyolefin system resin (a) ] [ the above-mentioned coating liquid ] Using a reverse roll coater, after a coating, it heat-treated for 60 seconds within a 100 \*\* hot air dryer continuously, and a lamination film was obtained. A lamination film was rolled round in the state of the after-cooling roll.

[0093]A result in which thickness of a coat layer after dryness measured 2 micrometers and coat weight was 2.0g/m<sup>2</sup>.

[0094]Various evaluation results of an obtained lamination film are shown in table-1. Acrylic modification urethane resin was manufactured like the work example 1 using the materials of the quantity shown in table-1 using the same device as the two to work-example 6 work example 1. The obtained acrylic modification urethane resin solution (base resin solution) is as 35 weight % of resin solid content concentration, the viscosity of this resin solution, and the weight average molecular weight of resin being shown in table-1.

[0095]Prepare coating liquid like the work example 1 using each base resin solution, and like the work example 1 Next, the substrate film made of polyolefin form resin.

(however, in the work examples 2-4, coating processing was performed for (having used c)) in (b) and the work example 6 in (a) and the work example 5, and the lamination film was obtained. The lamination film was rolled round in the state of the after-cooling roll.

[0096]The result in which the thickness of the coat layer after dryness measured 2 micrometers and coat weight was  $2.0\text{g/m}^2$ .

[0097]The various evaluation results of the obtained lamination film are shown in table-1.

Mix poly acrylic resin particle (bridge construction polymethyl-methacrylate-resin particles) 5 weight section (about 12 weight %) of 2 micrometers of mean particle sizes, it was made to distribute to base resin solution 100 weight section of 35 weight % of resin solid content concentration obtained in work-example 7 work example 1, and acrylic modification urethane resin solution (base resin solution) was obtained.

[0098]Next, coating liquid was prepared like the work example 1 using this base resin solution, coating processing was performed to the substrate film made of polyolefin form resin (a) like the work example 1, and the lamination film was obtained. The lamination film was rolled round in the state of the after-cooling roll.

[0099]The result in which the thickness of the coat layer after dryness measured 2 micrometers and coat weight was  $2.0\text{g/m}^2$ .

[0100]The various evaluation results of the obtained lamination film are shown in table-1.

Acrylic modification urethane resin was manufactured like the work example 1 using the materials of the quantity shown in table-1 using the same device as the comparative example 1 and the three work examples 1. The obtained acrylic modification urethane resin solution (base resin solution) is as 35 weight % of resin solid content concentration, the viscosity of this resin solution, and the weight average molecular weight of resin being shown in table-1.

[0101]Next, coating liquid was prepared like the work example 1 using each base resin solution, coating processing was performed to the substrate film made of polyolefin form resin (a) like the work example 1, and the lamination film was obtained. The lamination film was rolled round in the state of the after-cooling roll.

[0102]The result in which the thickness of the coat layer after dryness measured 2 micrometers and coat weight was  $2.0\text{g/m}^2$ .

[0103]The various evaluation results of the obtained lamination film are shown in table-1.

Comparative example 2 stirrer, a channeling-back condensator, a tap funnel, and a thermometer in the attached 4 TSU mouth flask Methylmethacrylate 280 weight section, 2-hydroxyethyl methacrylate 35 weight section, 2-ethylhexyl acrylate 35 weight section,

and methyl-ethyl-ketone 585 weight section were taught, it heated at 70 °C under the nitrogen air current, azobis isobutyronitrile 4.2 weight section was added, and it was made to react for 10 hours.

[0104]The obtained acrylic resin solution (base resin solution) was viscosity 300 mPa-s of 35 weight % of resin solid content concentration, and this resin solution, and the weight average molecular weight 16000 of resin.

[0105]Next, coating liquid was prepared like the work example 1 using this base resin solution, coating processing was performed to the substrate film made of polyolefin form resin (a) like the work example 1, and the lamination film was obtained. The lamination film was rolled round in the state of the after-cooling roll.

[0106]The result in which the thickness of the coat layer after dryness measured 2 micrometers and coat weight was 2.0g/m<sup>2</sup>.

[0107]The various evaluation results of the obtained lamination film are shown in table-1.

[0108]

[Table 1]

表-1

	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	比較例1	比較例2	比較例3
ウレタン樹脂原料仕込量(重量部)	31.4	25.1	18.8	31.5	31.5	31.5	31.4	44.0		31.4
ポリカーボネートジオール	128.4	102.6	76.9	128.8	128.8	128.8	128.4	180.1		128.4
グリセリンモノメタクリレート	2.2	1.8	1.3				2.2	3.1		2.2
2-ヒドロキシエチルメタクリレート				1.7	1.7	1.7				
メチルヒドロキノン	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.02		0.02
イソプロパノール	8.7	7.0	5.2	8.8	8.8	8.7	8.7	12.3		8.7
ジ- <i>n</i> -ブチルアミン	3.3	2.7	2.0	3.3	3.3	3.3	3.3	4.7		3.3
メチルエチルケトン	208.9	166.9	125.1	208.9	208.9	208.9	208.9	293.1		208.9
イソプロパノール	52.2	41.7	31.3	52.2	52.2	52.2	52.2	73.3		52.2
メチルメタアクリレート	38.1	36.1	36.1	36.1	36.1	36.1	36.1	36.1		36.1
メチルメタアクリレート	44000	44000	44000	44000	44000	44000	44000	44000		44000
2-ヒドロキシエチルメタクリレート	157.9	192.6	227.1	157.9	157.9	157.9	157.9	88.4	280	174.1
2-エチルヘキシルアクリレート	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.2	35	
アクリル成分(重量部)	5.2	6.3	7.3	5.2	5.2	5.2	5.2	3.1	4.2	5.2
メチルエチルケトン	385.4	437.2	488.9	385.4	385.4	385.4	385.4	281.6	585	385.5
アクリル樹脂/アクリル成分(重量比)	50/50	40/60	30/70	50/50	50/50	50/50	50/50	70/30	6/100	50/50
アクリル樹脂/アクリル成分(重量比)	20	20	20	20	20	20	20	20	20	0
アクリル樹脂/アクリル成分(重量比)	47000	40000	31000	45000	45000	45000	47000	65000	16000	47000
樹脂固形分濃度(重量%)	35	35	35	35	35	35	35	35	35	35
粘度(mPa·s)	500	300	100	450	450	450	500	32000	300	500
ポリアクリル樹脂粒子(重量部)							5			
評価結果										
引張強度	1100	1500	1800	800	800	800	1200	300	2200	400
基材フィルム	(a)420	(a)420	(a)420	(b)600	(b)600	(c)700	(a)420	(a)420	(a)420	(a)420
出(塗膜/基材フィルム)	2.6	3.6	4.3	1.9	1.3	1.1	2.3	0.7	5.2	0.9
ネッキング	○	○	○	○	○	○	○	○	△	○
耐摩耗性	○	○	○	○	○	○	○	○	×	○
耐傷付き性	4	5	4	4	4	4	5	1	4	2
耐水性	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好
SUV 600h照射	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好
SWOM 4000h照射	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好
								グロス低下	クラック発生	塗膜剥離
								汚れ付着	変色なし	汚れ付着

[Effect of the Invention]The lamination film made of polyolefin system resin of this invention can perform the same processing and handling as a polyvinyl chloride resin film, and any performances of many of curved surface flattery nature, a sex with a crack-proof, solvent resistance (gasoline-proof nature), and weatherability are excellent. It can be conveniently used as a film for adhesion films for an ornament (tape), such as a sticker aiming at attachment on the adhesion film the object for Medical Science

Division, and for industry (tape), a signboard, several kinds of parts, etc., and a marking film.

.....

.....

[Translation done.]